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Title:	Thermochemical and Thermophysical properties for the system of Ce metal and Ce hydride (deuteride)
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Thermochemical and Thermophysical properties for the system of Ce metal and Ce hydride (deuteride)

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- Knowledge of these properties is necessary in order to properly build a physics based model of the Ce ejecta evolution (conversion) in high pressure hydrogen gas
- Experimental measurements and corroboration with theory
- Knowledge of properties across phase space of the dynamic experiments:
    - Temperatures up to 1500K + if possible
    - Gas pressures from vacuum to ~ 8 atm (~100 atm in shocked condition)

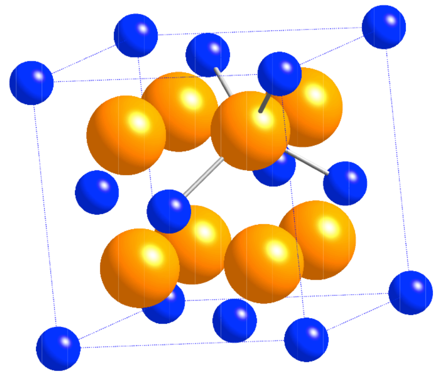
<u>Properties desired as a function of temperature</u>

- Ce – hydrogen – CeH_x phase diagram at higher temperatures
- Ce and CeH_2 heat capacity (specific heat)
- Ce and CeH_2 thermal conductivity
- Ce and CeH_2 coefficient of thermal expansion (CTE)
- Reaction enthalpy $Ce + H_2 \rightarrow CeH_{2+x}$, $\Delta H = 206$ kJ/mol
- CeH_2 melting temperature
- CeH_2 optical emissivity
- Diffusion of H in CeH_{2+x}
- Reaction rates $Ce + H_2 \rightarrow CeH_{2+x}$
- Mechanical properties of CeH_2

Hypothesis: reactive conversion

$Ce + H_2 \rightarrow CeH_{2+x}$ $\rightarrow$ other processes leading to particle breakup

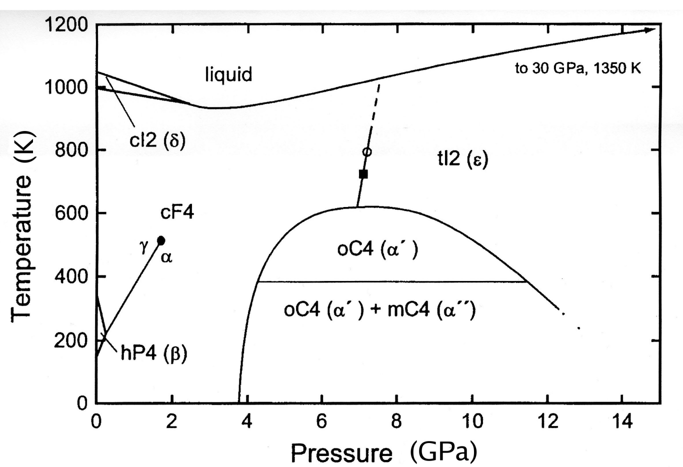
$Ce + H_2 \rightarrow$

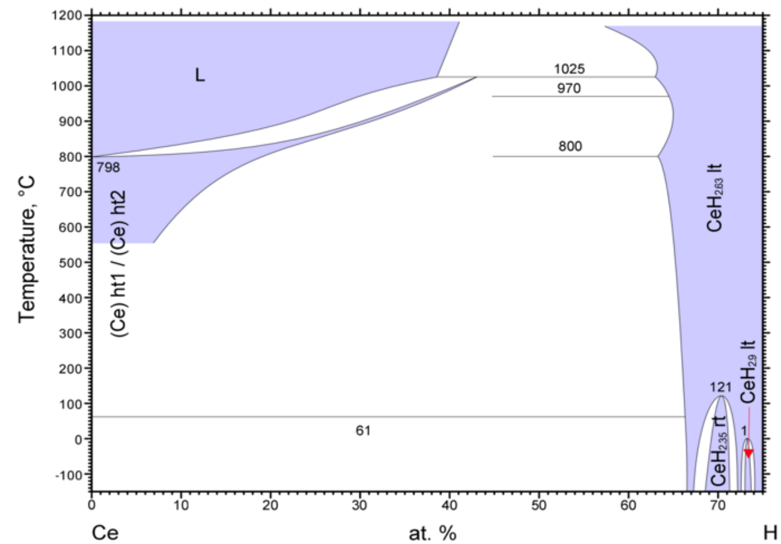


CeH_2

Fluorite crystal structure unit cell of CeH_2. Blue spheres represent Ce and orange spheres H. For the dihydride, all the tetrahedral sites in the FCC base Ce lattice are fully occupied, and for the higher (CeH_{2+x}) stoichiometries, the octahedral sites become occupied.

liquid Ce > 1071K
δ-Ce >999K bcc
γ-Ce >263K fcc

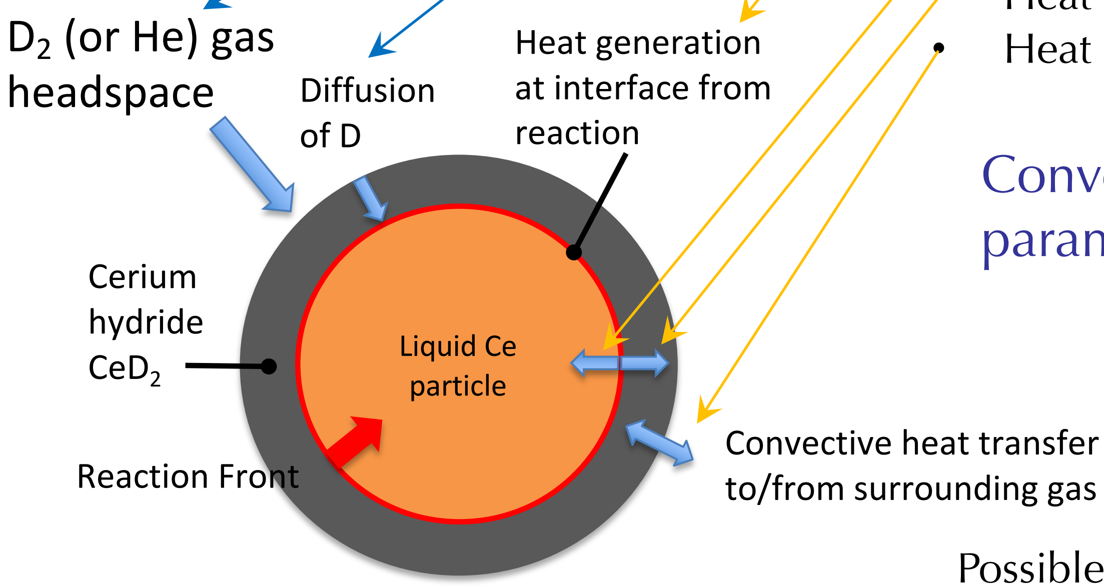




Conceptual view of the early stage of hydriding

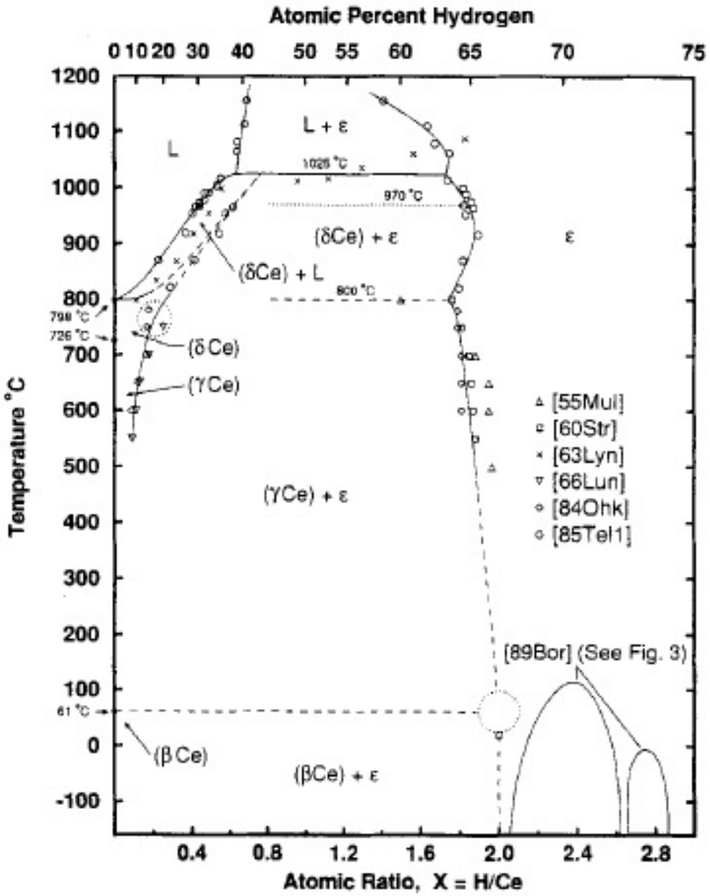
$$f = \frac{P}{\sqrt{2\pi MkT}}$$

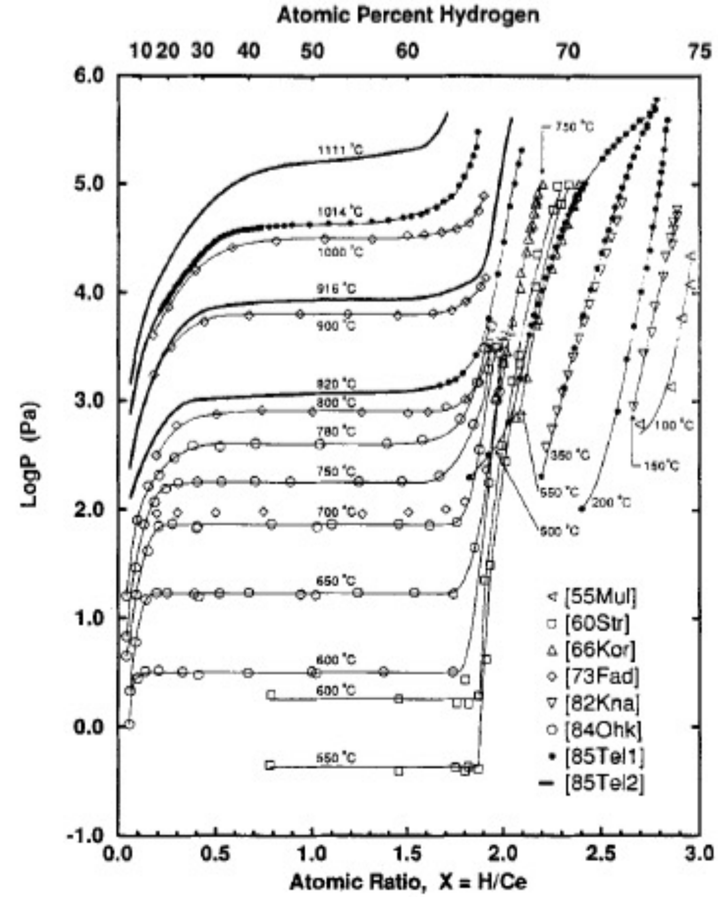
- Gas delivery (kinetic gas theory)
- Transport of reactant to interface (hydrogen diffusion)
- Reaction at interface Ce + 2D → CeD_2 + ΔH_f
- Reaction kinetics Ce + 2D → CeD_2
- Exothermic heat generation ΔH_f = -206 kJ/mol
  - Heat flow into Ce metal center: C_p(Ce), K(Ce)
  - Heat flow into CeD_2 skin: $C_p(CeD_2)$, $K(CeD_2)$
  - Heat partition into gas: $C_p(D_2)$, $K(D_2)$



Conversion process: parameters needed for model

Possible other factors
- Reaction volumetric change +26%
- Melting temperature of CeD_2
- CTE for Ce and CeD_2
- Mechanical properties of hydride





F.D. Manchester and J.M. Pitre, The Ce-H (Cerium-Hydrogen) System, Phase Diagram Evaluations: Section II, J. Phase Equil. Vol. 18 No. 1, 1977, 63-77.

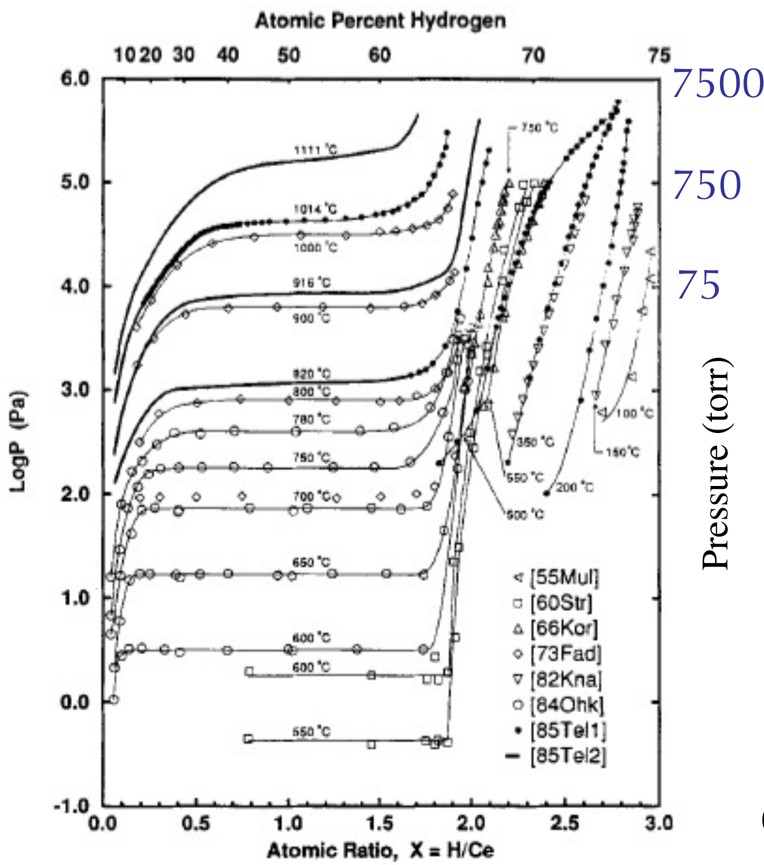
ε is the CeD_{2+x} phase. This phase is stable in the two phase field from D/Ce=0.2 and higher. The ε phase is stable at higher temperatures from D/Ce≅1.8 to ≅2.8, where the trihydride forms. Note that the CeD_2 phase remains solid under the right D_2 pressure conditions to at least 1200°C (1473K). It is important that we determine the melting temperature of CeD_2. Melting point might be in excess of 2000K based on similar structure Ce compounds (CeO_2).

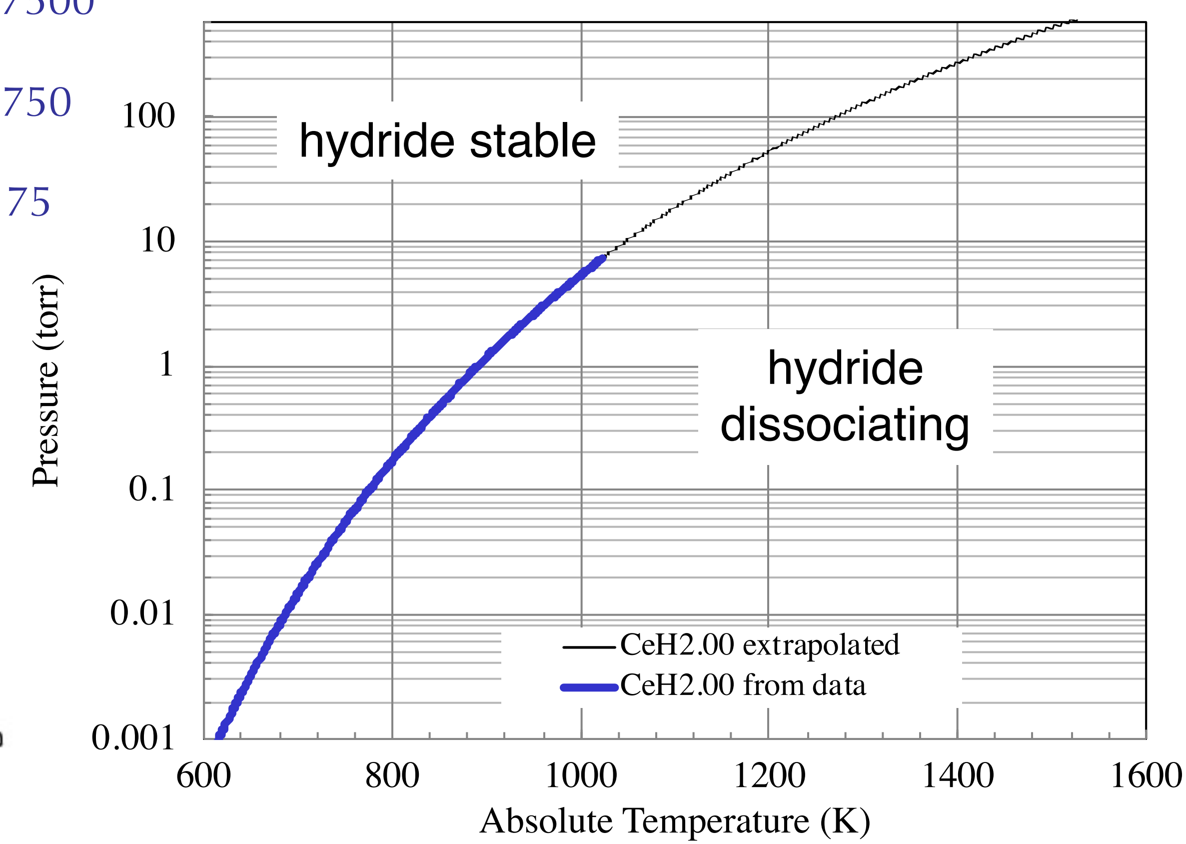
CeH_2 melting temperature of 1353 K (1080°C), likely not correct

L.I. Osadchaya, et. al., Preparation of Cerium Hydrides, Inorganic Materials, 39, 11, 2003, 1142-1143.

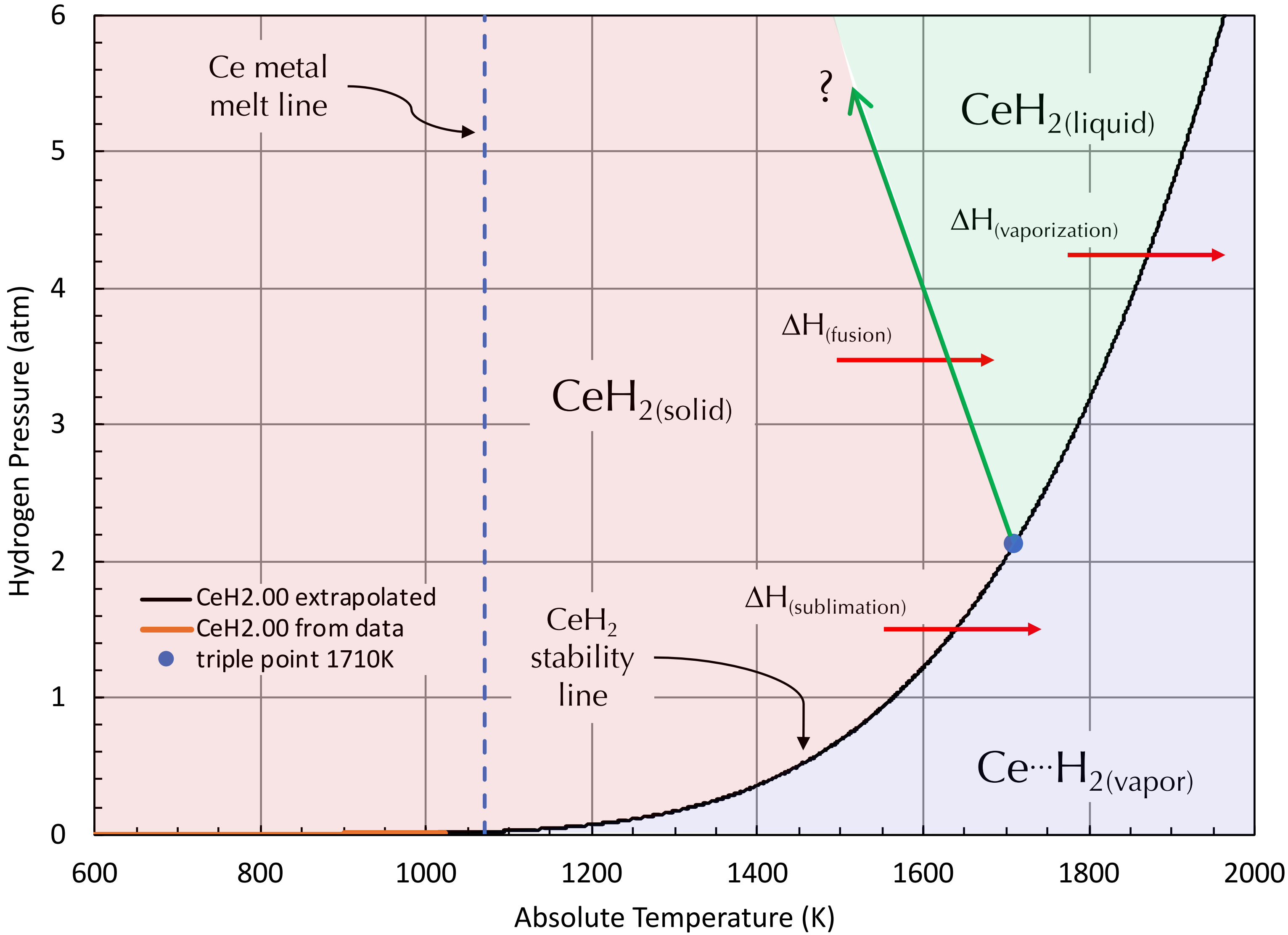
Conversion process:
Thermal stability of hydride product

$$Ce + D_2 \leftarrow\rightarrow CeD_2 + \Delta H_f$$





Conversion process: Thermal stability of hydride product



Conversion process: Thermal stability of hydride product

- The unary P-T phase diagram of CeH_2
- The CeH_2 P-T stability line (extrapolated from data) becomes the boundary between CeH_2 solid and vapor phases and the CeH_2 liquid and vapor phases. This makes sense since the once the CeH_2 is no longer stable (loss of hydrogen and conversion towards Ce metal liquid) the temperature is high enough to cause vaporization of the Ce.
- The triple point is estimated using the melting point of CeF_2 at 1710K
    - CeF_2 is has the same crystal habit (structurally identical) as CeH_2
    - CeF_2 is isoelectronic to CeH_2 – the configuration is (Ce^{3+}, $2H^-$, e^-) which leads to a metallic-behavior hydride
- I don't know the direction/shape of the CeH_2 solid – liquid boundary (most likely more vertical than I have it drawn)
- $\Delta H_{sublimation} > 0$ endothermic (will cool the system)
- $\Delta H_{fusion} > 0$ endothermic (will cool the system)
- $\Delta H_{vaporization} > 0$ endothermic (will cool the system)
- $\Delta H_{sublimation} = \Delta H_{fusion} + \Delta H_{vaporization}$
- For Ce metal $\Delta H_{sublimation}$ = 420 kJ/mol literature value
- The process of $CeH_{2(s)} \rightarrow Ce\cdots H_{2(g)}$ can be broken down as:
    - $CeH_{2(s)} \rightarrow Ce_{(s)} + H_{2(g)}$ + 206 kJ/mol
    - $Ce_{(s)} \rightarrow Ce_{(g)}$ + 420 kJ/mol
    - Total maximum of 626 kJ/mol possible required for the sublimation process of CeH_2 depending on what the final gas phase products are ($CeH_{2(g)}$ or $Ce_{(g)}$ and $H_{2(g)}$) – cooling power
    - Regardless of the nature of the gas phase products this would definitely be (atomic/molecular) and couple to the gas